



Review

Gastrophysics: Statistical thermodynamics of biomolecular denaturation and gelation from the Kirkwood-Buff theory towards the understanding of tofu



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ABSTRACT

Sugars, alcohols, or salts, when added to food, affects the heat denaturation of proteins and the sol-gel transition of macromolecules. Such an effect of cosolvents has long been known and exploited; yet understanding how they work at a molecular level has been a matter of scientific debate for decades, because of the lack of a definitive theory which can provide a microscopic explanation. Here we show that a rigorous statistical thermodynamic theory, the Kirkwood-Buff (KB) theory, provides not only a long-awaited microscopic explanation but also a clear guideline on how to analyze experimental data. KB theory synthesizes the classical Wyman-Tanford formula and partial molar volume, and enables the determination of biomolecule-water and biomolecule-cosolvent interactions solely from experimental data. Nothing beyond the materials in introductory physical chemistry or chemical thermodynamics textbooks is necessary to follow the derivations presented in this review.

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Abbreviations: KB, Kirkwood-Buff.

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1. Statistical thermodynamics for food science: why necessary?

Our aim is to convince the readers that statistical thermodynamics is indeed a useful tool for food science. This is especially

true, when we try to understand what is really happening at a molecular scale. Molecular-based understanding is central to food science, because it attempts to elucidate the texture and taste of food based upon its microscopic behaviour, i.e., the structure and interaction of the constituent molecules (Belitz, Grosch, & Schieberle, 2009; de Man, 1999; Walstra, 2003; Nishinari & Fang, 2016). Statistical thermodynamics, then, is indispensable, because it is the only branch of science which can provide a link between the microscopic and macroscopic worlds (Ben-Naim, 2006; Hill, 1956).

Applying statistical thermodynamics to complex systems such as food is far from being straightforward. Most commonly, two strategies have been adopted: (i) computer simulation (Barker & Grimson, 1989; Euston, Ur-Rehman, & Costello, 2007; Fundo, Quintas, & Silva, 2015) and (ii) development of simple models (van der Sman, 2016; van der Sman, Paudel, Voda, & Khalloufi, 2013). Simulations (such as molecular dynamics and Monte Carlo) implement statistical thermodynamics numerically. Simple model-based approaches are drawn chiefly from the models of polymers, surfaces, and colloids. The crux of the both approaches lies in the elegance of approximations, aimed at grasping the essence of molecular structure and interactions out of the overwhelming complexity of food systems.

In contrast to the above, we take an alternative approach: (iii) rigorous theory as a tool to extract molecular-level information from thermodynamic data. This approach is distinct from (i) and (ii) in that certainty, credibility and clarity of interpretation are guaranteed by the rigorous nature of the theory, because the theory comes directly from the Laws of Physics (Booth, Abbott & Shimizu, 2012; Booth, Omar, Abbott & Shimizu, 2015; Shimizu, 2004; Shimizu & Abbott, 2016; Shimizu & Boon, 2004; Shimizu & Matubayasi, 2014c; Shimizu, 2015; Stenner, Matubayasi, & Shimizu, 2016).

The aim of this review is to demonstrate how useful statistical thermodynamics is. We will derive all the necessary formulae from scratch. The derivation is quite straightforward; no background knowledge is required beyond introductory chemical thermodynamics, such as Gibbs-Duhem and Clausius-Clapeyron equations (Atkins & de Paula, 2014, pp. 680–682).

2. Thermodynamics without statistical mechanics is prone to confusion

Our proposal to apply rigorous statistical mechanics to food science does not mean in any way that we are advocating the abolition of the current thermodynamic and calorimetric approaches. On the contrary, statistical mechanics fulfils the full potential of thermodynamic analysis, by bringing in an unprecedented interpretive clarity at a molecular level. (Such a combination of thermodynamics and statistical mechanics is commonly called statistical thermodynamics; our standpoint is to pursue food(-related) science within the framework of statistical thermodynamics.) What have instead been abolished are confusion and ambiguity caused by the lack of an explicit molecular basis (Shimizu, 2004; Shimizu & Boon, 2004; Shimizu & Matubayasi, 2014a).

Question: Consider the addition of extra molecular component(s) – such as sugars, salts, amino acid derivatives, or macromolecules – to food. Such an addition of cosolvents affects gelation, solubility, denaturation, and aggregation. How do cosolvents modulate such equilibria? (Note that such extra components are referred to in many different names, such as cosolvents, cosolutes, additives, or solutes; “cosolvents” will be used throughout this paper.)

A thermodynamic answer: Consider a transition $\alpha \rightarrow \beta$ of the solute (referred to as species u), such as sol \rightarrow gel, solute in pure phase \rightarrow solute dissolved in solvent, folded \rightarrow unfolded, or monomers \rightarrow aggregate, and the accompanying the standard Gibbs free energy $\Delta\mu_u^*$. (Throughout this paper, Δ signifies the change that accompanies a transition $\alpha \rightarrow \beta$.) The addition of cosolvents (species 2) into water (species 1) changes the water activity, and therefore the chemical potential of water μ_1 . How $\Delta\mu_u^*$ changes with μ_1 can be expressed as a *competition* between the change in number of water and cosolvent molecules bound to the biomolecules, ΔN_{u1} and ΔN_{u2} (Fig. 1) that accompany the transition:

$$-\left(\frac{\partial\Delta\mu_u^*}{\partial\mu_1}\right)_{T,P,n_u \rightarrow 0} = \Delta N_{u1} - \frac{n_1}{n_2}\Delta N_{u2} \quad (1)$$

where n_1 and n_2 are bulk concentrations of water and cosolvent (Casassa & Eisenberg, 1964; Parsegian, Rand, & Rau, 1995; Parsegian, Rand, & Rau, 2000; Schellman, 1987; Tanford, 1968, 1969, 1970; Timasheff, 1998, 2002a, 2002b; Wyman, 1948; 1964). For example, ΔN_{u1} in the context of protein unfolding signifies $\Delta N_{ui} = N_{ui}^u - N_{ui}^f$, which corresponds to the difference in the number of bound water between the unfolded state (u) and the folded state (f).

Eq. (1) is commonly referred to as the Wyman-Tanford formula, whose interpretation owes to the seminal contributions by Wyman, Eisenberg, Tanford, Schellman, Timasheff, and Parsegian (Casassa & Eisenberg, 1964; Parsegian et al., 1995, 2000; Schellman, 1987; Tanford, 1968, 1969, 1970; Timasheff, 1998, 2002a, 2002b; Wyman, 1948; 1964;). Eq. (1) can readily be, and has indeed been, applied to interpret thermodynamic data (Baier, Decker, & McClements, 2004; Miyawaki & Tatsuno, 2010; Miyawaki, Dozen, & Nomura, 2013; Miyawaki, Omote & Matsuhira, 2015). All one should do is to plot $\Delta\mu_u^*$ against μ_1 (or equivalently against $RT \ln a_1$ where a_1 is the water activity (Atkins & de Paula, 2014, pp. 680–682)) in order to obtain $\Delta N_{u1} - \frac{n_1}{n_2}\Delta N_{u2}$ (Fig. 2). The food science applications of this formula include the effects of sugars, salts and alcohols on the thermal denaturation of proteins, as well as on gelation (Baier et al., 2004; Miyawaki & Tatsuno, 2010; Miyawaki et al., 2013; Miyawaki et al., 2015).

Further simplification: Which is the dominant contribution to the equilibrium shift, the change of water binding (ΔN_{u1}) or cosolvent binding (ΔN_{u2})? The Wyman-Tanford formula (Eq. (1)) on its own does not provide a definitive answer to this question. Yet dialysis measurements show that sugars, polyols, and “kosmotropic” salts are preferentially excluded from biomolecular surfaces (Fig. 1(b)) (Timasheff, 1998, 2002a, 2002b). Consequently they are not bound to biomolecules; hence the change of the bound number is zero, i.e., $\Delta N_{u2} = 0$ (Parsegian et al., 1995, 2000). This renders Eq. (1) a powerful tool by simplifying it to

$$-\left(\frac{\partial\Delta\mu_u^*}{\partial\mu_1}\right)_{T,P,n_u \rightarrow 0} = \Delta N_{u1} \quad (2)$$

The change in number of bound water molecules ΔN_{u1} , which accompany folding, gelation, solubilisation, aggregation, can therefore be measured directly from the Wyman-Tanford plot (Fig. 2) (Parsegian et al., 1995, 2000).

Controversy: Eq. (2) was the focus of the intense controversy, because of the unrealistically large numbers of water molecules have been estimated to be released from protein-ligand binding and allosteric transitions (Timasheff, 1998, 2002a). In the course of controversy, the following doubts have been raised about Eq. (1) (Parsegian et al., 2000; Timasheff, 1998, 2002a):

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